ChemComm
www.rsc.org/chemcomm

Interplay of anions and ligands on the nature and reducibility of NiO_x/Al_2O_3 catalysts prepared by impregnation

F. Negrier,*[a] E. Marceau[a] and M. Che[ab]
[a] *Laboratoire de Réactivité de Surface (UMR CNRS 7609), Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France. E-mail: negrier@ccr.jussieu.fr*
[b] *Institut Universitaire de France*

Received (in Cambridge, UK) 1st March 2002, Accepted 17th April 2002
First published as an Advance Article on the web 30th April 2002

When NiO_x/Al_2O_3 catalysts (Ni wt% = 1.5) are prepared by impregnation using $[NiL_2(H_2O)_2]X_2$ as precursors (L = diamine, X = Cl^- or NO_3^-), a supported oxidic or metallic phase can be selectively obtained after thermal treatment in N_2 depending on the nature of the ligand and counter anion; the oxidic phase can be reduced at a lower temperature than the classical nickel aluminate phase obtained from $[Ni(H_2O)_6](NO_3)_2$.

NiO_x/Al_2O_3 are widely used for the production and conversion of syngas.[1] Depending on the gas needed (H_2, CO, CO_2, CH_4, *etc.*), an oxidic[2] or a metallic[3] nickel phase is used: the design of the final catalyst is achieved by thermal treatment in an oxidizing (O_2, air) or/and reducing (H_2) atmosphere. The major problem encountered in the preparation by impregnation of NiO_x/Al_2O_3 catalysts is the migration of Ni(II) ions into the alumina lattice during calcination to form $NiAl_2O_4$-like species.[4] Nickel aluminates are known to be poorly active for several types of oxidation and hydrogenation processes.[5,6] Furthermore, they are difficult to reduce and as a result, the obtention of metal particles requires high temperature and long thermal treatments leading to sintering of the metallic phase.[7]

In the past years, some studies of our laboratory have focused on the advantages of using chelating diamine ligands to prepare catalysts by ion exchange.[8,9] Diamine ligands give hydrosoluble, stable and easy-to-obtain nickel complexes. They provide an interesting alternative for the deposition of highly dispersed ionic species leading to catalysts suitable for various types of applications (olefin oligomerization, CO hydrogenation, *etc.*).[10,11]

These results led us to investigate the effect of commercial aliphatic diamines such as 1,2-ethanediamine (en, $C_2H_6N_2$) and *trans*-1,2-cyclohexanediamine (tc, $C_6H_{14}N_2$) in the preparation of NiO_x/Al_2O_3 catalysts by incipient wetness impregnation. This technique, which consists in filling the pore volume of alumina with an aqueous solution of nickel salt and subsequent drying, is the most common way to prepare nickel catalysts because of its simplicity and enables the control of the amount of deposited complexes. At the same time, it forces the couter anions of the salt to remain on the support and their further interactions with nickel and ligands during the transformations of the catalyst can not be neglected. Nitrate, generally used in the preparation of nickel catalysts, and chloride were selected as counter anions of the Ni(II) precursor complexes.

In the present study, four catalysts have been prepared with the following precursor salts: (EnC) $[Ni(en)_2(H_2O)_2]Cl_2$, (EnN) $[Ni(en)_2(H_2O)_2](NO_3)_2$, (TcC) $[Ni(tc)_2(H_2O)_2]Cl_2$ and (TcN) $[Ni(tc)_2(H_2O)_2](NO_3)_2$. These precursors have been synthesized using hexaaquanickel(II) nitrate and the corresponding diamines (Aldrich) as described earlier.[12,13] The pore volume of γ-alumina (IFP EC1285, specific surface area 200 $m^2\ g^{-1}$, pore volume 0.6 mL g^{-1}) was filled with an aqueous solution of the precursor salt (C_{Ni} = 0.38 M) and the humid solid was dried in air at 100 °C for 10 min. The resulting solids (Ni wt% = 1.5) were treated in N_2 up to 500 °C (7.5 °C min^{-1}, 2 h at 500 °C) and further characterized by diffuse reflectance UV-Vis-NIR and DRIFT *in situ* spectroscopies between 20 and 500 °C, Temperature programmed reduction (TPR), XRD and TEM. The gases produced were analyzed by mass spectrometry (MS).

DOI: 10.1039/b202203f

After drying and heating of the catalysts at 230 °C in N_2 for 10 min, elemental analyses of Ni, C, N and Cl were in agreement with ligand/nickel and anion/nickel ratios of 2. The counter anions and ligands remain with Ni(II) ions on the alumina surface. UV-Vis-NIR spectra of catalysts EnC, EnN and TcC exhibit four similar intense absorption bands (catalysts En: I = 8330, II = 9900, III = 15060, IV = 25640 cm^{-1}; catalyst TcC: I = 8260, II = 9950, III = 15150, IV = 25700 cm^{-1}) which can be interpreted as a grafted pseudotetrahedral complex $NiN_2(OAl)_2$, by comparison with the results on the unsupported solid $[Ni(en)Cl_2]$.[14] DRIFT spectroscopy shows the presence of $R–NH_2$ vibrations at 3252–3317 cm^{-1} and $R–NH_3^+$ vibrations at 3038–3050 cm^{-1}, also observed when diamines are adsorbed on alumina. However, no desorption of ligands was detected by MS below 230 °C, which is in contradiction to what occurs with diamines adsorbed alone on alumina. It can be concluded that the two ligands are probably bridging every Ni(II) ion and the alumina surface as shown in Scheme 1.

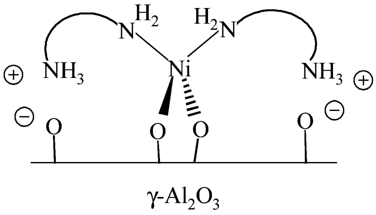
For catalyst TcN, four bands are detected (I = 8800, II = 14100, III = 18520 and IV = 29700 cm^{-1}) which are in agreement with the formation of an adsorbed complex *trans*-$[Ni(tc)_2(NO_3)_2]$ on the basis that their positions and intensities are similar to those recorded for the unsupported solid *trans*-$[Ni(tc)_2(NO_3)_2]$.[15]

The above results show that, after a 10 min treatment at 230 °C in N_2, the diamines remain bonded to adsorbed Ni(II) ions, inhibiting the migration of the latter into alumina.

At higher treatment temperatures and in the case of chlorides (catalysts EnC and TcC), the formation of hydrochloric acid upon desorption was detected by a silver nitrate test. According to MS, hydrogen was produced at 400 °C (m/z = 2) and accompanied by the appearance of a C=N imine vibration band at 1655 cm^{-1} on DRIFT spectra.

The ligand thus undergoes a β-hydrogen elimination from the amine groups. For tc, richer in hydrogen than en, an additional dehydrogenation of the cyclohexane ring led to the desorption of aniline (m/z = 93). In these cases, the diamine chelating ligand acts as a hydrogen source bonded to Ni(II) ions.

In the case of nitrates (catalysts EnN and TcN), the desorption of oxidation products (CO, H_2O, NO) at 300 °C is detected by MS and suggests that nitrates oxidize the organic ligands. In the case of catalyst TcN, both ligand oxidation and hydrogen production were observed (Fig. 1).



Scheme 1 Grafted Ni(II) complex after thermal treatment of catalysts EnC, EnN and TcC (230 °C in N_2, 10 min).

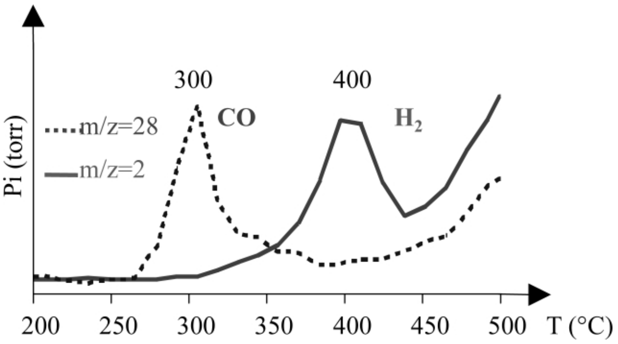


Fig. 1 MS thermograph of dried catalyst TcN.

After treatment of catalyst EnC at 500 °C in N_2 for 2 h, a broad band is observed in the visible region (12500–25000 cm^{-1}) which corresponds to the reduction of Ni(II) ions to the metallic state. The TPR profile of sample EnC shows hydrogen consumption at 500 °C with a ratio $[H_2]/[Ni] = 0.5$: the autoreduction of the complex is partial. When tc is used as chelating ligand in the presence of either chloride or nitrate (catalysts TcC and TcN), the reduction of Ni(II) ions to the metallic state is also evidenced by UV-Vis spectroscopy. TPR/MS experiments recorded on these samples only show hydrogen consumption due to the methanation of carbon traces. The autoreduction of these systems is total and leads to ~3 nm diameter nickel particles detected by XRD and TEM.

When nitrate and en are used (catalyst EnN), an ionic Ni(II) phase is detected by UV-Vis spectroscopy (bands at 25000 and 31250 cm^{-1}). Its UV-Vis signature is different from those of octahedral (24100 cm^{-1}) and tetrahedral (15700 and 16800 cm^{-1}) Ni(II) ions in a $NiAl_2O_4$ phase obtained in the same conditions using nickel nitrate as precursor. This result shows that en chelating ligands prevent the formation of nickel aluminates during the catalyst treatment at 500°C in N_2. The TPR experiment on sample EnN shows that Ni(II) ions obtained are reduced at 500 °C with a ratio $[H_2]/[Ni] \sim 1$. Hydrogen consumption also observed by TPR at 850 °C is due to the methanation of adsorbed residual carbon (MS, $m/z = 15$). An aluminate phase prepared in the same conditions for the same nickel content is reduced at 950 °C according to the TPR measurements with a ratio $[H_2]/[Ni] = 0.6$, compared with a quantitative reduction of the ionic phase at 500 °C for catalyst EnN. As a consequence, a one-hour reduction of the aluminate at 950 °C leads to 15–60 nm nickel particles while 2–5 nm particles are obtained by reduction of catalyst EnN at 500 °C (Fig. 2).

According to the results concerning catalysts EnC, TcC and TcN, the hydrogen liberated upon decomposition of the ligands reduces Ni(II) ions to metal: aliphatic diamines act as reducing agents. However, the total reduction of Ni(II) to metallic particles in presence of either counter anion (nitrate or chloride) is complete only with a H-rich ligand such as tc (catalysts TcC and TcN). In contrast, nitrate ions (catalyst EnN) act as an oxygen reservoir which burns the ethanediamine ligand and an ionic Ni(II) phase is obtained. Additionally, chelating diamines act as stabilizing agents that prevent both the migration of Ni(II) ions into the alumina lattice and the formation of $NiAl_2O_4$. This stabilizing effect of the ligand has strong repercussions on the reducibility of the catalysts.

In conclusion, this work shows that the species (ligand and counter anion) deposited with nickel upon impregnation can be used either separately or synergetically, *via* their redox properties, to selectively obtain an ionic Ni(II) and/or a metallic nickel phase after thermal treatment in N_2. Furthermore, the use of chelating ligands as stabilizing agents inhibits the formation of $NiAl_2O_4$ and strongly increases the Ni(II) reducibility. The interplay of counter anions and H-containing chelating ligands in the nickel precursor complex opens up new possibilities in the preparation of supported catalysts by impregnation.

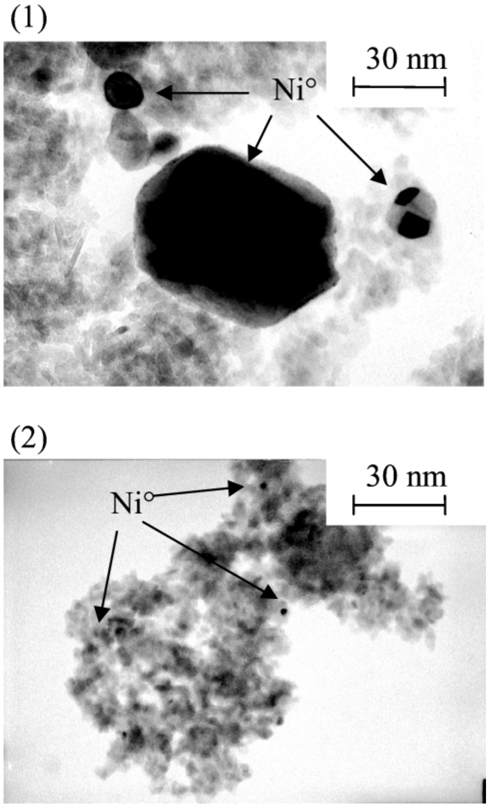


Fig. 2 TEM micrographs of the H_2-treated catalysts $[Ni(H_2O)_6]/Al_2O_3$ at 950 °C (1) and EnN at 500 °C (2).

Notes and references

1 Z. Xu, Y. Li, J. Zhang, L. Chang, Z. Rongqi and Z. Duan, *Appl. Catal. A*, 2001, **210**, 45.
2 Q. Miao, G. Xiong, S. Sheng, W. Cui, L. Xu and X. Guo, *Appl. Catal. A*, 1997, **154**, 17.
3 K. O. Xavier, R. Sreekala, K. K. A. Rashid, K. K. M. Yusuff and B. Sen, *Catal. Today*, 1999, **49**, 17.
4 J. M. Rynkowski, T. Paryjczak and M. Lenik, *Appl. Catal. A*, 1993, **106**, 73.
5 D. Dissanayake, M. P. Rosynek, K. C. C. Kharas and J. H. Lunsford, *J. Catal.*, 1991, **132**, 117.
6 K. B. Kester and J. L. Falconer, *J. Catal.*, 1984, **89**, 380.
7 J. Zielinski, *J. Catal.*, 1982, **76**, 157.
8 J. Y. Carriat, M. Che, M. Kermarec, M. Verdaguer and A. Michalowicz, *J. Am. Chem. Soc.*, 1998, **120**, 2059.
9 Z. X. Cheng, C. Louis and M. Che, *Stud. Surf. Sci. Catal.*, 1995, **91**, 1027.
10 M. Che, C. Louis and Z. X. Cheng, *J. Am. Chem. Soc.*, 1995, **117**, 2008.
11 Z. X. Cheng, C. Louis and M. Che, *Stud. Surf. Sci. Catal.*, 1993, **75**, 1785.
12 N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 1964, **4**, 804.
13 K. J. Gerard, J. Morgan, P. J. Steel and D. A. House, *Inorg. Chim. Acta*, 1997, **260**, 27.
14 G. De, P. K. Biswas and N. R. Chaudhuri, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3145.
15 Y. Ihara, Y. Fukuda and K. Sone, *Inorg. Chem.*, 1987, **26**, 3745.